Photo-cured
Organic-Inorganic Nano-Hybrid Materials
- Preparation and Optical properties -

Kimihiro MATSUKAWA
Osaka Municipal Technical Research Institute
Joto-ku, Osaka 536-8553, Japan

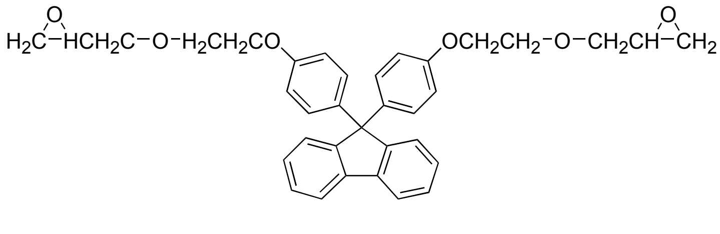
Introduction

Organic-inorganic nano-hybrids are molecularly dispersed nano-composites of organic and inorganic components, which are noted as most attractive materials with improved properties compared to each single materials. These are expected to become new functional materials for versatile advanced applications. Nano-hybrids can be prepared by a sol-gel reaction of metal alkoxides and organic polymers, with some interactions such as covalent bonding[1-5], hydrogen bonding[6,7], π-π interaction[8] and so on. However, as some amount of alcohol and water are generated by the hydrolysis and condensation of metal alkoxides during a sol-gel reaction for the formation of inorganic components, it is difficult to produce the thicker film of organic-inorganic nano-hybrids because of a generation of crack by shrinking the hybrid materials during the completion of the sol-gel reaction. Furthermore, the sol-gel reaction needs longer time and heat treatment. For resolving these disadvantages, we have studied the preparation of organic-silica nano-hybrids using photo-curable silsesquioxanes which are nano-sized functional materials prepared by the sol-gel reaction of organic substituted trialkoxysilane and expected to generate the novel hybrid materials.

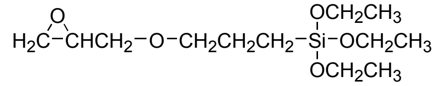
The different combinations of organic and inorganic components have been available in hybrid materials, that there is a great potential for the electrical, optical, structural applications, etc. Especially, as the organic-inorganic nano-hybrid thin films are optically transparent, they are useful materials for optical devices. High refractive index is the most important property for optical applications such as flat panel display devices, opto-communications, etc. It is well-known that organic materials with aromatic ring or sulfur element and inorganic substances such as titania and zirconia have higher refractive index. Therefore, organic-inorganic nano-hybrids with these components are interesting materials which can control their refractive index by changing the composition ratio. In this work, the organic-inorganic nano-hybrid thin films were prepared by photo-cationic polymerization and thiol-ene reaction using photo-curable silsesquioxanes, and the refractive index of nano-hybrid thin films was evaluated. These nano-hybrids could make the turnable refractive index thin films with different composition ratio of organic- and inorganic-components.

Photo-cured nano-hybrids with bis-phenyl fluorene derivatives

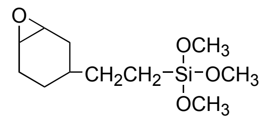
As aromatic ring compounds provide high refractive index, fluorene is interesting molecules for optical materials. Bisphenoxyethanolfluorene diglycidylether (BPEFG) has high refractive index (1.62), and the unique "Cardo" structure of isotropic four benzene rings attached on 9-position of fluorene cause low birefringence and heat resistance. In order to synthesize the organic-inorganic nano-hybrid with fluorene, it is necessary to interact between BPEFG and the silsesquioxanes[9]. Epoxy groups of epoxytrialkoxysilanes are polymerized with BPEFG and benzene ring of phenyltrialkoxysilane can generate the π-π interaction with fluorene ring. Therefore, co-silsesquioxanes were prepared by the the



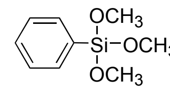
BPEFG



GPTES

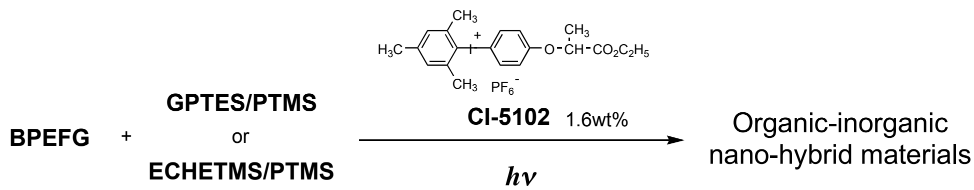


ECHETMS



PTMS

co-condensation of glycidoxypropyl triethoxysilane (GPTES) or epoxycyclohexylethyl trimethoxysilane (ECHETMS) and phenyltrimethoxysilane (PTMS). Co-silseaquioxanes, GPTES/PTMS and ECHEMS/PTMS, were obtained as the clear THF solutions without any formation of gels. However, as the existence of silanols was recognized from the FT-IR spectra, the condensation was not completed under this reaction condition. Photo-cationic polymerization of these silsesquioxanes and BPEFG was carried out with CI-5102 as photo-acid generator (PAG)[10], shown in **Scheme 1**. The FT-IR spectra of organic-inorganic hybrid thin films of BPEFG with ECHETMS/PTMS before/after UV irradiation and after PEB are shown in **Figure 1**. The spectrum of after UV irradiation indicates that a broad peak at about 900 cm^{-1} from epoxy groups changed weak, compared with the spectrum of before irradiation. Although the characteristic peak of silanol exists also in this area of wavenumbers, it is barely to confirm the progress of photo-cationic polymerization. The peak of O-H stretching of silanol at 3400 cm^{-1} was reduced, and it was found that the condensation of silanols occurred under UV irradiation. The PAGs can function as an acid catalyst of sol-gel reaction, as well as we have reported that photo-induced sol-gel reaction of epoxytrialkoxysilane progressed simultaneously with photocationic polymerization of epoxy groups[11]. It was found that the condensation of silanols was completed after PEB at 150˚C for 1.5 hours.



Scheme 1

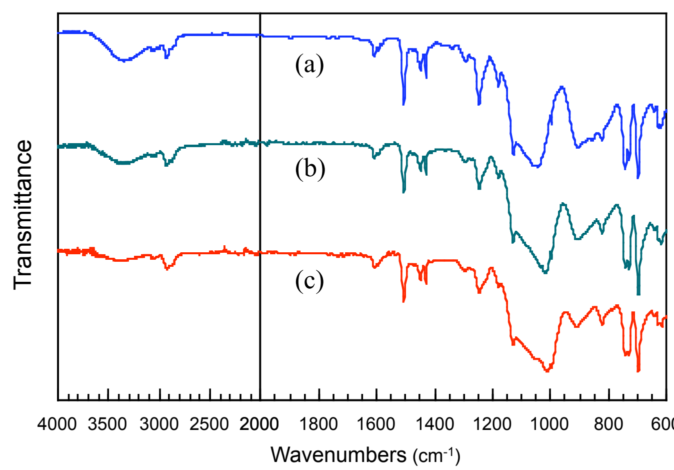


Figure 1. FT-IR spectra of organic-inorganic hybrids of BPEFG with ECHETMS/PTMS (composition ratio 1/1) (a) before UV irradiation, (b) after UV irradiation (1300mJ/cm^2), (c) after PEB (150 ˚C, 1.5 hours).

The organic-inorganic nano-hybrid thin films thus obtained was clear and transparent. UV-vis absorption spectrum of these organic-inorganic nano-hybrid thin film (thickness 5μm) of BPEFG with ECHETMS/PTMS showed high transmittance over 95% in a visible region. These organic-inorganic nano-hybrids are also expected to be relatively high refractive index, which is summarized in Table 1.

The refractive index of hybrid thin films showed slightly low with increasing composition weight ratio of epoxysilsesquioxanes for BPEFG. On the other, the refractive index of GPTES and ECHETMS were 1.43 and 1.45 respectively. Therefore, the BPEFG-inorganic hybrid thin films with ECHETMS/PTMS indicated higher refractive index than that with GPTES/PTMS.

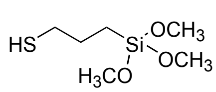
Table 1. Refractive index of organic-inorganic hybrid thin films of BPEFG and epoxysilsesquioxanes.

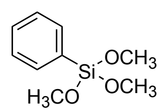
Composition weight ratio			Thickness(nm)	Refractive index
BPEFG	GPTES/PTMS	ECHETMS/PTMS		
1	0	0	100	1.62
1	1	0	98	1.59
1	0	1	90	1.60
2	1	0	84	1.61
2	0	1	89	1.62

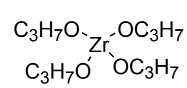
Some mechanical properties of these nano-hybrid thin films were evaluated. In the case of pencil hardness test for a surface hardness, the hybrid thin films containing a large amount of silseaquioxane were harder than a mere cured BPEFG. And also, the surface condition of nano-hybrid thin films had no cracks, it was estimated that silsesqioxane relaxed the shrinkage of epoxy polymerization.

Photo-cured nano-hybrids containing sulfur compounds

It is well-known that refractive index of sulfur compounds is higher than usual organic compounds, so the nano-hybrids containing sulfur compounds are very interesting optical materials. This sort of nano-hybrids were prepared by a thiol-ene reaction as photo-polymerization containing sulfur elements. The thiol-ene reaction, which is a radical addition reaction of thiol group to C=C bond, is an attractive photo-curing system with low shrinkage and no inhibition by oxygen[12]. Therefore, thiol-ene reaction with thiol-containing silsesquioxanes and multifunctional allyl compounds was carried out without any photo-initiators[13]. The thiol-containing silsesquioxanes could be prepared from the condensation of mercaptopropyltrimethoxysilane with several reaction conditions, as summarized in **Table 2**. The co-condensed silsesquioxane with zirconium isopropylate and titanium isopropylate can be prepared for the higher refractive index nano-hybrids. Triallylisocianate(TAIC) as a multifunctional allyl compound was reacted with thiol-containing silsesquioxanes under UV irradiation, as shown **Figure 2**. The progress of reaction could be confirmed by reduction of -SH and allyl peaks in the Raman spectroscopy.


a


b


c

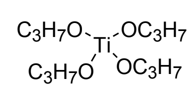

d

Table 2. Preparation of thiol-silsesquioxanes and their properties.

Silsesquioxane	Components (mol ratio)	Solid contents (%)	Solvents	Viscosity (mPa·s)	-SH equivalent (g/eq)
SQ-1	a	99	None	10000	135
SQ-2	a:b=2:1	99	None	100000	205
SQ-3	a:c=12:1	75	DME	300	190
SQ-4	a:d=15:1	50	DMDG	100	480

DME ： ethylene glycol dimethylether DMDG：diethylene glycol dimethylether

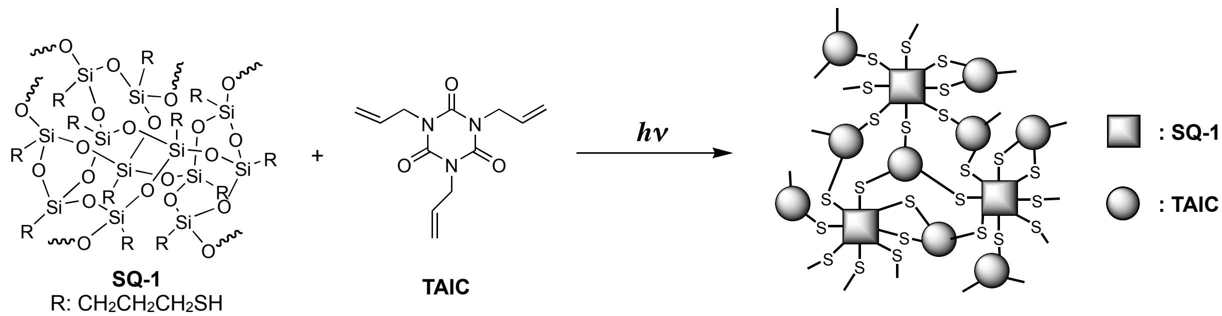


Figure 2. Reaction of sulfur containing nano-hybrid materials from SQ-1 and TAIC.

These nano-hybrid materials could make a thick film under UV irradiation and showed high transparency (transmittance >95% through 30μm film thickness). From **Table 3** summarized their properties, it was found that refractive index and Abbe number of nano-hybrid thin films are relatively high. These characteristics are very effective for optical applications. The light resistance was superior to the photo-cured acrylate because there was no coloration due to the decomposition of photo-initiators. And also, these hybrid materials had high heat resistance compared to usual thiol-ene cured non-hybrid materials.

Table 3. Properties of sulfur containing nano-hybrids with thiol-containing silsesquioxane and TAIC.

Silsesquioxane	Water absorption (25°C, 24hr)	Pencil hardness on glass	Coefficient of thermal expansion (ppm/°C) 40-45°C/150-155°C	Refractive index	Abbe number
SQ-1	0.7%	3H	111 / 171	1.56	46
SQ-2	0.7%	3H	102 / 164	1.56	42

Conclusion

The organic-inorganic nano-hybrids were prepared from photo-curable silsesquioxanes by the photo-cationic polymerization with bisphenoxyethanolfluorene diglycidylether and the thiol-ene reaction with tri-allyl compounds. These hybrids formed excellent transparent films, and their refractive index were relatively high, which is expected to apply for optical materials.

References

1. G. L. Wilkes, B. Orler, and H. Huang, *Polym. Prepr.* **26**, 300 (1985).
2. H. Schmidt, *J. Non-Cryst. Solids,* **73**, 681 (1985).
3. H. Schmidt and H. Wolter, *J. Non-Cryst. Solids,* **121**, 428 (1990).
4. B. Wang, G. L .Wilkes, C. D. Smith, and J. E. McGrath, *Polym. Commun.*, **180**, 428 (1990)
5. J. We and G. L. Wilkes, *Chem. Mater.*, **8**, 1667 (1995).
6. T. Saegusa and Y. Chujo, *J. Macromol. Sci. Chem.*, **A27**, 1603 (1990).
7. Y. Chujo, *Polym. Mater. Encycl.*, **6**, 4793 (1996).
8. R. Tamaki, K. Samura, and Y. Chujo, *Chem. Commun.*, 1131 (1998).
9. K. Matsukawa, Y. Matsuura, A. Nakamura, N. Nishioka, T. Motokawa, and H. Murase, *J. Photopolym. Sci. Technol.*, **19**, 89 (2006).
10. A. Shirai, H. Kubo, and E. Takahashi, *J. Photopolym. Sci. Technol.*, **15**, 29 (2002).
11. H. Inoue, K. Matsukawa, Y. Ishitani, and N. Nishioka, *J. Adhesion Soc. Jpn.*. **32**, 370 (1996).
12. A. F. Jacobine, Thiol-Ene Photopolymers in “Radiation Curing in Polymer Science and Technology”, Vol. III, Polymerization Mechanisms, Eds. J. P. Fouassier, J. F. Rabek, Elsevier Applied Science (1993).
13. K. Matsukawa, T. Fukuda, and H. Goda, *2007 MRS Spring Meeting,* Abstract Q3.1 (2007).